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Rheological Characterization of Gas Hydrate Formation Kinetics and Transportability in Crude Oil Slurries

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Abstract

Characterizing the ability of crude oils to naturally inhibit gas hydrate crystal growth and transport formed gas hydrates is critical when considering gas hydrate management strategies in the field. In this paper, a medium crude oil was investigated in a high pressure rheometer using a transient restart/shut-in method in order to determine important fluid properties in the hydrate formation thermodynamic region. An increase in subcooling temperature was found to increase the yield stress (due to increased hydrate volume fraction) and formation rate of gas hydrates in the slurry while decreasing the overall bulk fluid relative viscosity (due to the lower amount of unconverted water). Viscosity profiles in the non-plugging operation regime allow for a hydrate agglomeration and break-up mechanism involving dynamic gas hydrate particle/water droplet interaction forces to be presented in this work. Transient operation revealed gas hydrate formation during shut-in due to the establishment of the memory effect beforehand. The use of shear-controlled rheological measurements gives important insight into not only the bulk fluid properties of hydrate slurries, but also the mechanisms behind gas hydrate agglomeration and blockages.

Keywords

Gas Hydrates; Flow Assurance; Rheology

Introduction

Rheology has shown to be a beneficial tool when studying the complex fluid properties involved in crude oil/hydrate mixtures [1]. Important fluid parameters including viscosity, yield stress, and loss/storage modulus can be measured continuously throughout hydrate formation. Rheological information can then be combined with kinetic hydrate formation rates to build a clear characterization of overall fluid behavior. Previous work has shown that hydrate slurries exhibit shear-thinning non-Newtonian behavior [1]. The mechanism of shear thinning is thought to be a function of particle size and particle interaction forces. The extent to which shear can disperse formed gas hydrates within slurries is then linked to the action of natural surfactants present in oils. Natural surfactants (such as asphaltenes and resins) reduce the cohesive force between hydrate particles [2] [3]. Thorough quantification of rheological properties during the process of hydrate formation and subsequent dispersion or agglomeration can give valuable insight into the overall non-plugging behavior of crude oils.

A less conventional gas hydrate kinetics and growth measurement can be coupled with flowability measurements to reinforce non-plugging predictions. In this case, intuition for gas hydrate crystal growth kinetics can be drawn from previous film growth measurements taken from the surface of single cyclopentane hydrate particles [4]. The natural surfactants within crude oils can also act as kinetic hydrate inhibitors (KHIs), causing a reduction in initial crystal growth rate upon hydrate nucleation. The quantification of *in-situ* growth kinetics is a powerful tool for further characterization of the non-plugging potential of crude oils.

Methodology

Fluid Properties

Table 1 depicts the properties of the crude oil tested in this work. All experiments were conducted using a 3.5 wt.% sodium chloride brine. The hydrate forming gas was a mixture of 25.3 mol% ethane and 74.7 mol% methane.

Table 1. Crude Oil Properties and Composition

Property	Value
°API	23.4
Saturates (wt.%)	47.5
Aromatics (wt.%)	44.8
Resins+Asphaltenes (wt.%)	7.9

Experimental Setup

Rheology experiments were carried out using a high-pressure cell equipped with a 4-blade vane style impeller as seen in Figure 1.

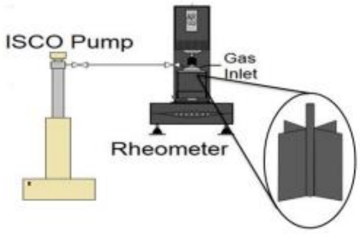

Figure 1. Experimental setup for high-pressure rheology experiments (adapted from [5])

Experimental Procedure

All experiments were conducted using a pre-emulsified sample at 30 vol.% water cut. Emulsions were prepared using a high-speed homogenizer operating at 8000 rpm at ambient pressure and temperature. The continuous phase (oil) was measured into a container and the dispersed phase (water) was added dropwise during the first 1.5 minutes of stirring. The emulsion was then allowed to stir for an additional 1.5 minutes. After the emulsion was added to the pressure cell, the procedure given in Figure 2 was followed for rheological measurements.

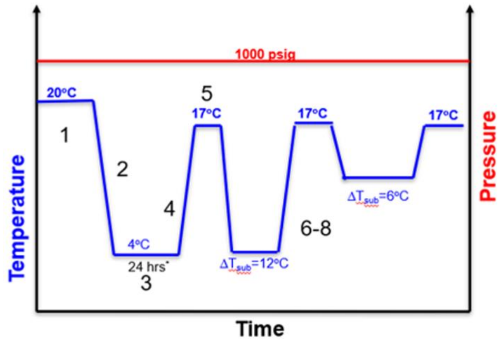

Figure 2. Experimental pressure and temperature conditions for rheology experiments

It is important to note that these experiments involve hydrate formation to induce the memory effect as well as a transient shut-in step. The memory effect is useful because it reduces stochasticity involved with hydrate nucleation and produces results that are more consistent.

Table 2. Experimental Matrix

Test	Water Cut (vol.%)	Subcooling (°C)
1	30	12*
2	30	12
3	30	6

* Performed without memory effect

Table 2 displays the conditions for experiments performed in this study.

Results and Discussion

Table 3. Rheology Results for Experiments Conducted at 30 vol.% Water Cut

Variable	Test 1	Test 2	Test 3
Subcooling (°C)	12*	12	6
Relative Viscosity (Peak)	10.0	9.6	49.1
Hydrate Volume Fraction	0.3	0.3	0.1
Conversion (vol.%)	96	87	57
Yield Stress (Pa)	-	6.9	38.7
Initial Growth Rate (g/L*hr)	45	93	31

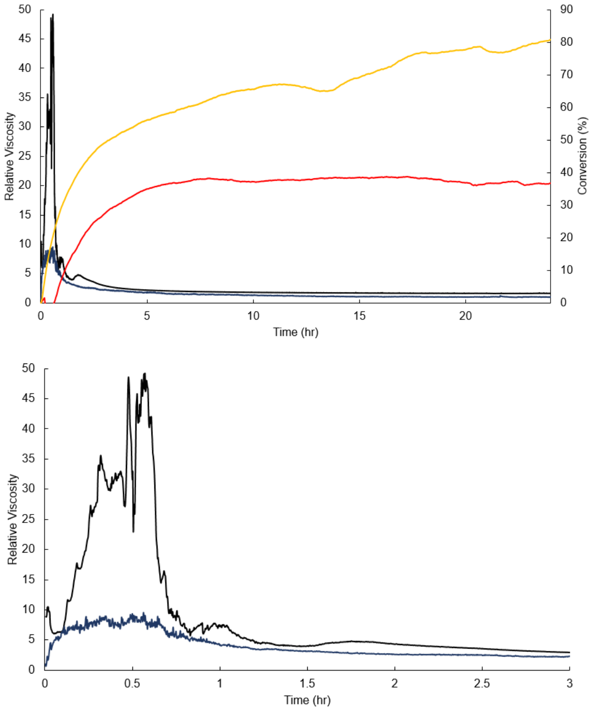

Figure 3. **a)** Relative viscosity (blue) and conversion (yellow) as a function of time for test 2 and relative viscosity (black) and conversion (red) as a function of time for test 3. **b)** Relative viscosity for test 2 (blue) and test 3 (black) during the first 3 hours. Time zero refers to the beginning of restart (after shut in) in both cases.

Table 3 and Figure 3 display results obtained for experiments conducted at 30 vol.% water cut. The general shape of the viscosity profile seen in Figure 3 is a hallmark of hydrate formation. The hypothesis is that as gas hydrates begin to form, there is an initial increase in viscosity to a peak value followed by a subsequent decay to a steady state value. This profile is explainable through a gas hydrate/water droplet agglomeration/breakup mechanism. During initial stages of formation, forces between water droplets and hydrates shells dominate, which have been shown through high-pressure micromechanical force measurements to be significantly higher than hydrate particle-particle interactions [6].

It is important to note that there was measureable water conversion to hydrate during the shut-in period (17 and 20 vol.% for tests 2 and 3 respectively) and these values are included in the overall conversion value given in Table 3. As subcooling decreases from 12 to 6°C, relative viscosity at the peak increases from 10.0 to 49.1, which is consistent with the idea that more capillary bridging exists between gas hydrate particles at lower subcooling due to the larger amount of unconverted water. Steady state relative viscosity increases from 0.98 to 1.6 when subcooling is lowered from 12 to 6°C.This phenomenon is further supported by the increase in yield stress from 6.9 to 38.7 Pa observed in tests 2 and 3 respectively, despite the lower conversion value in test 3. Overall, lower subcooling values increase the average interparticle/water droplet forces due to the larger amount of unconverted water.

Finally, initial growth rate was measured (as seen in Table 3) to quantify the effect of both the memory effect and subcooling on gas hydrate formation kinetics. Each growth rate was measured during the first 5 minutes of hydrate formation after nucleation occurred (as indicated by a distinct increase in viscosity). The growth rate increased from 45 g/L*hr in test 1 to 93 g/L*hr in test 2, showing that the memory effect and hydrates formed during shut in increase the rate of initial growth by about 2 times. The growth rate decreased from 93 g/L*hr in test 2 to 31 g/L*hr in test 3, which aligns with the intuition that lower driving force causes a decrease in hydrate formation rate.

Conclusions

In this work, the natural ability of a medium crude oil to disperse gas hydrates was quantified through rheological kinetics and transportability experiments. It was shown that an increase in subcooling temperature lowers the overall viscosity of the fluid, but increases the initial rate of gas hydrate formation. The memory effect was shown to produce more consistent results with regard to nucleation time but also increases the rate of initial gas hydrate formation. The gas hydrate formation during transient shut-in operation was also attributed to the presence of the memory effect. Further experimentation and characterization as shown in this work will help to guide hydrate management strategies and risk tolerance in the field.

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Responsibility Notice

The authors are the only responsible party for the paper content.

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